

Chapter 1

Biochar as a Sustainable Resource to Drive Innovative Green Technologies

Joan J. Manyà^{*,‡} and Gabriel Gascó[†]

**Escuela Politécnica Superior, Aragón Institute of Engineering Research (i3A), Universidad de Zaragoza, Huesca, Spain*

†School of Agricultural, Food and Biosystems Engineering, Technical University of Madrid, Madrid, Spain

‡joanjoma@unizar.es

Abstract

An overall vision of the biochar science and technology is given in this chapter. The emerging applications of biochar in electrochemical energy storage and catalysis, as well as its environmental applications within the scope of the circular economy, are described. The use of biochar as carbon sequestration technology, the benefits of its utilization as growing media component or its possible use for the recovery of contaminated soils are treated in this chapter. Special attention is focused on highlighting the need to gain knowledge on the links between feedstock properties, production process and conditions and possible uses of biochar. This becomes essential to guide research and technology toward the production of engineered biochars with the best properties to be used in a given application.

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1.1 Introduction

There are many definitions about the concept of biochar. Lehmann and Joseph defined biochar as a carbon-rich solid obtained by the thermal decomposition of organic matter under a limited supply of oxygen and at relatively low temperatures [Lehmann and Joseph, 2009]; the International Biochar Initiative defines biochar as a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment [IBI, 2015] while the European Biochar Certificate [Delinat Institute, 2013] defines biochar as a char produced by pyrolysis for use in agriculture (and other non-thermal applications) in an environmentally sustainable manner. According to this last definition, the solid fraction obtained by thermal treatments as torrefaction or hydrothermal carbonisation (HTC) (solid fraction is named hydrochar) cannot be called biochar [Delinat Institute, 2013] although the solid fraction can have a similar end use in agriculture or for other environmental purposes.

Chars can be prepared from biomass with different origins as agriculture and forestry, gardens, kitchens or canteens or other wastes as biosolids [Méndez *et al.*, 2012; Paz-Ferreiro *et al.*, 2012], paper fiber sludge [Méndez *et al.*, 2009] or different types of manure [Cárdenas-Aguar *et al.*, 2019; Gascó *et al.*, 2018] with several environmental advantages. For example, the application of biochar to the soil can imply the reduction of emissions of CO₂ and greenhouse gases as methane and nitrous oxide emissions (Table 1.1). Traditionally, the main application of biochar has been its application to agricultural soils to increase crop production. The enhancement of agricultural production is due to the improvement of physical, chemical and biological soil properties. For example, biowaste-derived biochar can increase the soil water holding capacity and improve the structural stability of soil [Méndez *et al.*, 2012], increase both cation exchange capacity (CEC) and pH of soil and nutrient content [Paz-Ferreiro *et al.*, 2012]. Also, there are several studies describing how chars can improve biological properties of soils [Gascó *et al.*, 2016; Paz-Ferreiro *et al.*, 2012, 2016] contributing to improved soil quality. On the other hand, the production of biochar and its storage in soils have been suggested as a technology for abating climate change by sequestering carbon estimation such that the total net emissions of CO₂ could be reduced over the course of a century by 130 Pg CO₂ [Wolf *et al.*, 2010].

Table 1.1: Environmental advantages of biochar soil application.

Agricultural use

1. Carbon sequestration: Reduction of CO₂ emissions.
2. Reduction of methane and nitrous oxide emissions.
3. Positive effect in chemical soil properties: Increase in CEC, reduction in soil acidity and organic matter content.
4. Positive effect in physical properties: Improve water holding capacity, available water, field capacity and soil structure.
5. Increased microbiological activity.
6. Reduction of the amount of organic and inorganic fertilizers needed.
7. Increased quality and yield of crops.

Other advantages

8. Thermal treatment reduces the risk of presence of pathogens.
9. Adsorption of organic compounds: Reduction of bad smells.
10. Control of metals leaching.
11. Reduction of phosphate and nitrate pollution of streams and groundwater.
12. Good growing media to the plants.
13. Reduction of the volume of biowaste to transport to landfill.

1.2 Biochar and Soil Carbon Sequestration

The potential carbon sequestration in soil after biochar application relates with carbon stability of biochar, which depends on the raw material and pyrolysis conditions, mainly pyrolysis temperature. The conditions of biochar preparation have a great influence on the carbon content, type of organic compounds, whether it is easily oxidized, the organic carbon, volatile matter and fixed carbon that are related with the potential carbon sequestration in soil after biochar application. Bruun *et al.* [2011] observed that the cumulative CO₂ emissions from soil were reduced from 11% to 3% application of biochar from wheat straw prepared at 475°C and 575°C, respectively, according to the reduction of the biochar labile fraction with the increase in pyrolysis temperature.

Méndez *et al.* [2013] estimated that CO₂ emissions from a loamy soil after 10 years can be reduced after the application of biosolid-based biochars (rate: 8%) from 301 (pyrolysis temperature: 400°C) to 932 kg CO₂ ha⁻¹ (pyrolysis temperature: 600°C) with respect to the direct application of biosolids. Gascó *et al.* [2016] described, after the application of

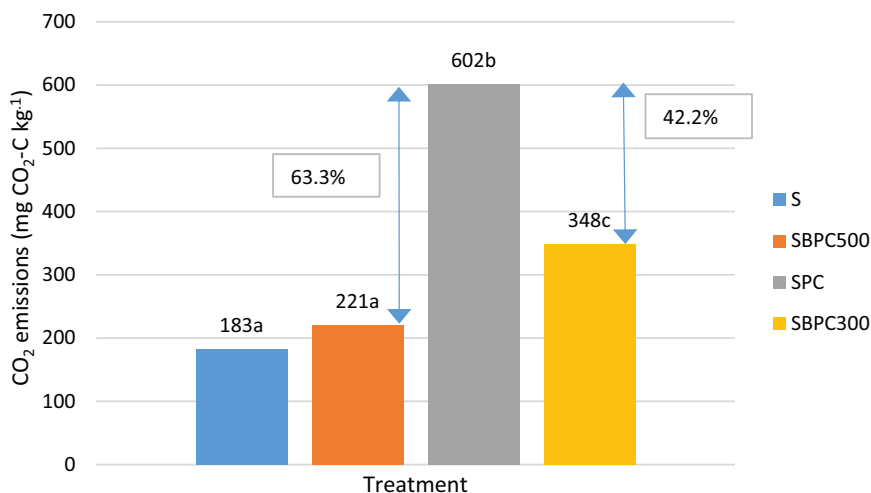


Figure 1.1: C mineralization of soil (S) after application of pig manure (SPC), pig manure biochar prepared at 300°C (SBPC300), pig manure biochar prepared at 500°C (SBPC500) at a rate of 8%. Values followed by the same letter are not significantly different ($P = 0.05$) using the Duncan test.

Source: Adapted from Gascó *et al.* [2016].

biochar prepared from pig manure at 300°C and 500°C, reductions of CO₂ emissions from 42.2% to 63.3% after 219 days and no differences between control soil (classified as Cambisols) and soil amended with the biochar prepared at 500°C (Figure 1.1). Apart of the carbon sequestration, the preparation of chars from organic waste as biosolids or manures, has other environmental benefits, such as the reduction of nitrogen leaching, the recovery of P and K [Wang *et al.*, 2012], reduction of the volume of waste material, improvement of both physical and biochemical soil properties [Liang *et al.*, 2014; Lu *et al.*, 2014] with important implications on agricultural production within the scope of the circular economy due to the valorization of organic wastes.

On the other hand, the pyrolysis may become more expensive due to high moisture content of some raw materials as biosolids, or pig slurry making, in these cases, the HTC more suitable due to it being a thermochemical process of organic matter conversion in the presence of water, under moderate temperatures (180–260°C) and autogenous pressures [Hiltzl *et al.*, 2015], as a result of which HTC requires minimal drying

compared with pyrolysis. The produced hydrochar can have a moderate heat value, high carbon content and mesoporous textures [He *et al.*, 2013] with different applications depending on thermal treatment conditions. Gascó *et al.* [2018] concluded that HTC of pig manures could be an interesting method to obtain soil growing media or green roof materials with adequate hydrophysical properties, whereas biochars obtained by pyrolysis of pig manure (Figure 1.2) could be used as soil amendments and that obtained at 600°C can be used for carbon sequestration due to its higher aromaticity.

However, the preparation of hydrochars is also a good strategy for the valorization of organic wastes and for the reduction of CO₂ emissions. Cárdenas-Aguilar *et al.* [2019] observed, during an incubation experiment of 60 days, a reduction of CO₂ emissions between 97.7% and 88.7% for biochars produced at 600°C and 450°C and between 68.8% and 59.0% for hydrochars produced at 240°C and 190°C, with respect to the incubation of a rabbit manure. This increase in carbon sequestration is related with the degree of organic matter humification and thermal stability after both

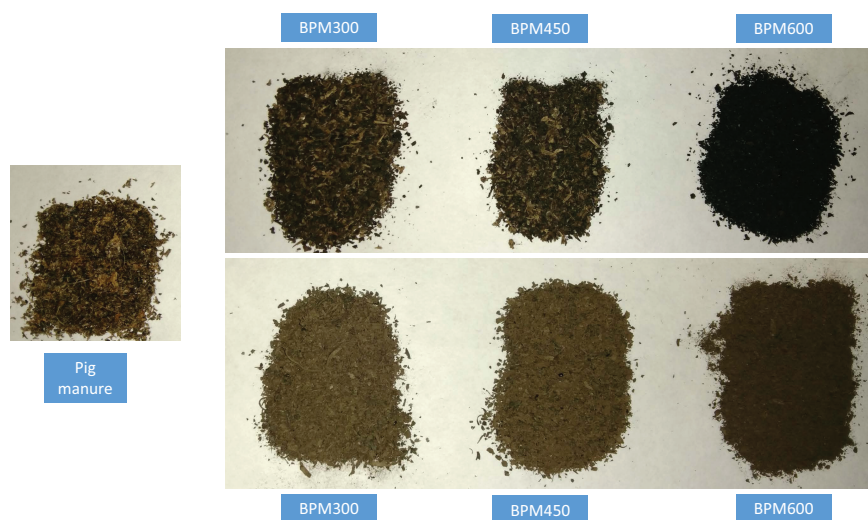


Figure 1.2: Pictures of biochars (BPM) and hydrochars (HPM) prepared from pig manure at different temperatures. Biochars: BPM300 (300°C), BPM450 (450°C), BPM600 (600°C). Hydrochars: HPM200 (200°C), HPM220 (220°C), HPM240 (240°C).

Source: Adapted from Álvarez [2019].

pyrolysis and HTC treatments. The difference between the CO₂ emissions between biochars and hydrochars is due to that pyrolysis produces chars with predominantly aromatic structures while HTC results in chars with a higher content in aliphatic structures according to the thermal stability of the materials. The importance of pyrolysis and HTC as carbon fixation technologies for adaptation and mitigation of climate change have been revealed by the roundtable “Biochar: the safe, scalable and shovel-ready carbon sequestration solution” organized by International Biochar Initiative and Husk Ventures in the last UN Climate Change Conference celebrated on December 2019 in Madrid.

1.3 Biochar as Component of Growing Media

More recently, the use of chars as components of growing media has emerged as a new use to reduce the pressure on peatlands, which cover an estimated area of 400 million ha, equivalent to 3% of the Earth's land surface. Peatlands globally represent a major store of soil carbon sink for carbon dioxide and source of atmospheric methane. For example, northern peatlands store around 450 billion metric tons of carbon, which is equivalent to approximately one-third of the global soil carbon stock, which is an important sink for carbon dioxide and source of atmospheric methane [Strack, 2008]. Peatlands are a resource that are not renewable at the human timescale, and nowadays there is a great deal of concern surrounding peatland protection and their overexploitation, which can cause, for example, the autoignition of peatlands (Figure 1.3) and the destruction of a non-renewable resource. For instance, there are necessarily 100 years required for the formation of between 0.8 and 12.1 cm of peat under Spanish weather conditions [Guerrero, 1987].

As growing media component, peat is mixed with components like vermiculite, perlite or clays. Indeed, the price of different growing media ingredients as perlite (50 €/m³), pumice (40–45 €/m³), clay (60 €/m³) or peat (25–40 €/m³), coupled with the above-mentioned environmental concerns, are pushing towards the use of alternative materials [Álvarez *et al.*, 2017]. Nevertheless, water holding capacity of biochar is lower than other common growing media components, i.e. peat, limiting their ability to fully replace growth substrates in horticulture. However, although biochars do not show adequate chemical and hydrophysical properties for



Figure 1.3: Autoignition of Zuacorta peatland (Spain) in 1985.

Source: Courtesy of F. Guerrero.

their individual use as growing media, their addition to peat in adequate rates could improve the chemical and physical properties of growing media and, as a consequence, the biomass production of different species [Nieto *et al.*, 2016; Méndez *et al.*, 2015]. Recently, biochar have been tested as growing media component with remarkable results when they are mixed with peat, including increases of yield over 100% [Nieto *et al.*, 2016; Méndez *et al.*, 2015]. Table 1.2 shows some relevant studies about the use of chars as growing media components.

Nevertheless, it is possible to obtain hydrochars from selected biomass by HTC with similar hydrophysical properties as peat. For example, Figure 1.4 shows how the water holding capacity curves at low suction values (until -10 kPa) of two hydrochars prepared from biosolids (HSL) and organic fraction of urban waste (HUW) are very similar to the curve of a commercial brown peat (PT). In this case, the HSL was thermally treated at $205\text{--}215^{\circ}\text{C}$ during 6 h and 17–19 bar, whereas HUW was treated at $190\text{--}200^{\circ}\text{C}$ during 6 h and at a pressure of 17–19 bar. The figure also shows that HSL presents a similar water retention curve to that of PT. Indeed, Álvarez *et al.* [2017] described increments of biomass production of *L. perenne* higher than 180% in growing media prepared with biosolids-derived hydrochar with respect to peat alone.

Table 1.2: Use of biochar/hydrochar as growing media component.

Feedstock	<i>T</i> (°C)	Crop	Treatments (% <i>, v/v</i>)	Yield (%)	References
Biochar as growing media component					
Organic fraction urban waste	270	Ryegrass	Peat	100	Gascó <i>et al.</i> [2018]
			Biochar	175	
			Peat + Biochar (50/50)	274	
Pruning waste	500	Lettuce	Peat	100	Nieto <i>et al.</i> [2016]
			Peat + Biochar (50/50)	200	
Deinking sludge	300	Lettuce	Peat	100	Méndez <i>et al.</i> [2015]
			Biochar	2	
			Peat + Biochar (50/50)	165	
Crushed wooden boxes	600	Sunflower	Biochar	100	Steiner <i>et al.</i> [2014]
			Peat	137	
			Biochar + Peat (25/75)	115	
			Biochar + Peat (50/50)	112	
			Biochar + Peat (75 + 25)	125	
Urban green waste	550	Wheat	Scoria (20% coir) + Biochar (70/30)	121	Cuong <i>et al.</i> [2014]
			Scoria (20% coir) + Biochar (60/40)	111	
			Scoria + Biochar (60/40)	111	
Green waste	160–220	Calathea	Biochar (100)	100	Tian <i>et al.</i> [2012]
			Biochar + Peat (50/50)	163	
			Peat (100)	133	
Hydrochar as growing media component					
Biosolids	190–200	Ryegrass	Peat	100	Álvarez <i>et al.</i> [2017]
			Biosolids hydrochar (50/50)	184	
			Peat + Biosolids hydrochar (50/50)	216	
Organic fraction urban waste	205–215	Ryegrass	Peat	100	Álvarez <i>et al.</i> [2017]
			Urban waste biochar (50/50)	100	
			Peat + Urban waste biochar (50/50)	100	

Furthermore, Gascó *et al.* [2018] have prepared hydrochars (range of temperatures: 220–240°C) from pig manures with water holding capacities higher than 66%, this value being between 523% and 595% higher than raw material and more than 200% higher than biochar prepared at 600°C. These authors related the higher water holding capacity with more volume of porous hydrochars in the range between 200 and 30,000 nm, which are related with water content of chars between 33 and 1500 kPa of pressure.

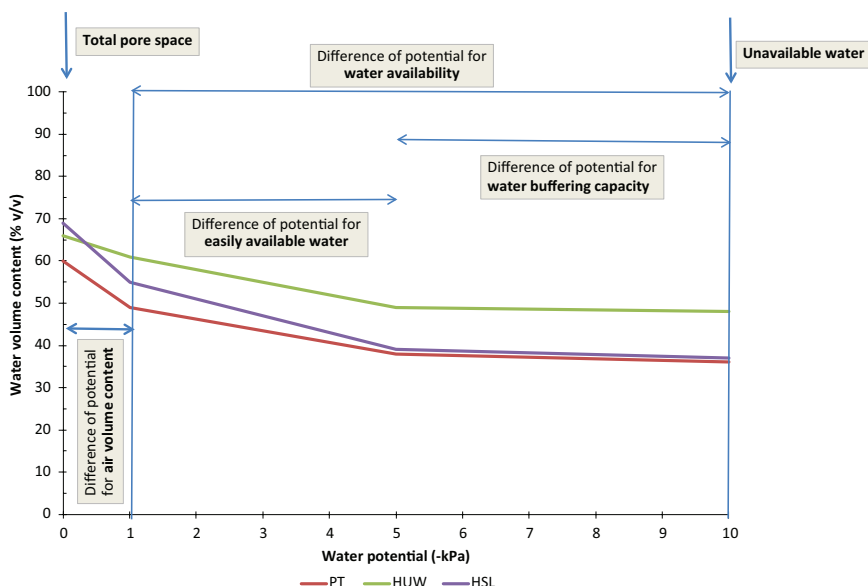


Figure 1.4: Water retention curves of hydrochars from biosolids (HSL) and organic fraction of urban waste (HUW) and a commercial brown peat (PT).

In summary, it could be possible to prepare hydrochars from selected biomass and adequate HTC conditions, which could have hydrophysical and chemical properties similar to those of peat with applications in the preparation of growing media or other environmental applications as recovery of contaminated or degraded soils.

1.4 Biochar for the Recovery of Contaminated Soils

In the last years, the use of biochar have received attention as soil amendment for the stabilization of organic and inorganic contaminants, with a great amount of studies carried out about this application [Méndez *et al.*, 2009; Sopena *et al.*, 2012]. With respect to heavy metals, different biochar properties as pH, CEC, presence of oxygenated surface groups, surface area or high content of $\text{Ca}^{2+}/\text{Mg}^{2+}$ are involved in the immobilization of heavy metals in soils, reducing their mobility and bioavailability [Méndez *et al.*, 2009; Paz-Ferreiro *et al.*, 2014; Uchimiya *et al.*, 2011] due to

different processes as precipitation, adsorption and exchange or modification of redox state of the trace metal. This fact together with the improvement of soil pH, CEC, both nutrient and organic matter content, water holding capacity or biological soil properties after biochar addition can be positive to the growth of phytoextractor increasing the metal extraction in multi contaminated soil [Paz-Ferreiro *et al.*, 2014]. This topic will be extensively addressed in Chapter 5, “Biochar Application for Mine Land Reclamation: Metal Mining”.

1.5 Emerging Applications of Biochar

Biochar-based materials can also be excellent candidates for applications in adsorption, catalysis and energy storage [Liu *et al.*, 2015]. Despite the fact that raw biochar has poor surface functionality (only some C–O, C=O and OH groups can be present) and very limited surface area (usually $< 150 \text{ m}^2\text{g}^{-1}$) [Mullen *et al.*, 2010], its porosity and surface chemistry can be relatively easily tuned for a given application, resulting in a very promising platform to synthesize valuable and tailor-made functional materials.

1.5.1 Biochar activation

To enhance the performance of biochar-based materials in adsorption or catalytic applications, a controlled porosity and a high surface area are desirable to facilitate high mass transfer fluxes and high active loading [Titirici *et al.*, 2012]. To this end, activated carbons having a hierarchical porosity (comprising macro-, meso- and micropores; as shown in Figure 1.5) can be produced from the raw biochar through either physical or chemical activation. During the physical activation process, the raw biochar is partly gasified with steam or CO_2 at temperatures ranging from 800°C to 1000°C . Physical activation usually leads to carbons having a well-developed microporosity with a very small contribution from mesoporosity [Liu *et al.*, 2015]. During chemical activation, the raw biochar is usually impregnated or mixed with alkali chemicals, such as KOH, and then heated under an inert gas environment at $600\text{--}800^\circ\text{C}$. The mass ratio KOH/biochar appears to be the most influential factor on the porosity of the resulting activated carbon. In this sense, a lower KOH dosage

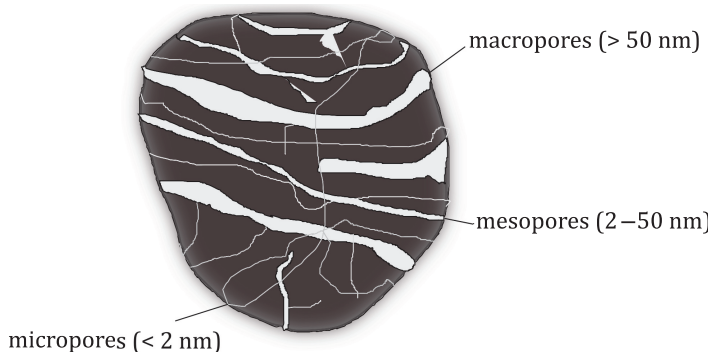


Figure 1.5: Schematic illustration of an activated carbon particle.

(e.g. a mass ratio KOH/biochar lower than 2) can promote the formation of micropores or ultra-micropores (<0.7 nm) with a narrow pore size distribution [Wei *et al.*, 2012]. On the contrary, increasing the KOH/biochar ratio can result in an increase in the specific surface area and total pore volume (with higher contribution from mesoporosity) as a consequence of pore widening [Li *et al.*, 2014].

As an alternative pathway to the two-step production of activated biochars (i.e. carbonization and subsequent activation), single-step production processes have recently received special attention, especially when hydrothermal conversion processes are involved. As an example of one-step process, one can mention the combined HTC and salt templating (e.g. by using eutectic salt mixtures) synthesis process as a very promising pathway to obtain carbon materials with an engineered micro- and mesoporosity [Alatalo *et al.*, 2016]. In addition, it should be highlighted that the introduction of heteroatoms (N,S) can also be conducted via single-step HTC processes. In this respect, S- or N-doped carbons can significantly improve the performance of biomass-derived carbon materials in many applications.

In addition to the effects related to the activation pathway and conditions, it should be kept in mind that the properties of the biochar precursor will also play a key role in determining the properties (both porosity and chemical functionalities in surface) of produced activated carbons. The physicochemical properties of biochar are mainly dependent on the

biomass feedstock as well as the kind and conditions of the thermochemical process applied.

1.5.2 Adsorption in aqueous phase

Several early studies were focused on using biochar-based activated carbons for the adsorption of several heavy metals in aqueous solutions, such as As(V) [Jin *et al.*, 2014], Cu(II) [Aguayo-Villarreal *et al.*, 2017; Zuo *et al.*, 2016], Hg(II) [Tan *et al.*, 2016] and Pb(II) [Ho *et al.*, 2017]. Adsorption mechanisms of metals on activated biochars mainly depend on the electrostatic interaction, ion-exchange, physisorption, and complexation and/or precipitation of functional groups [Tan *et al.*, 2017]. According to this, the most appropriate activated carbons for adsorption of heavy metals in wastewater seem to be those having a hierarchical pore size arrangement (with relatively high contributions from mesoporosity) [Aguayo-Villarreal *et al.*, 2017] with a considerable amount of oxygen-containing functionalities (e.g. hydroxyl and carboxylic groups) [Aguayo-Villarreal *et al.*, 2017; Tan *et al.*, 2017].

Biochar-based activated carbons also received special attention as promising adsorbents for removal of organic pollutants in aqueous phase. For this purpose, carbon-based adsorbents with highly developed mesoporosity are preferred, given the large size of the molecules involved (e.g. dyes and biomolecules) [Roldán *et al.*, 2016]. For the specific case of the adsorption of dyes, mesoporous carbons doped with nitrogen and/or sulfur can be synthesized through single-step HTC and salt templating. Alternatively, the introduction of heteroatoms and/or the salt templating steps can be conducted via activation of biomass-derived HTC chars. For instance, Liu *et al.* [2017] reported an excellent absorption capacity of acid orange 7 for a dual N,S-doped mesoporous carbon, which was produced via impregnation with ZnCl_2 of a sewage sludge-derived hydrochar.

1.5.3 Adsorption in gaseous phase

Adsorption of gases on biochar or biomass-derived carbons is a very promising alternative to storing them. The main advantages of these renewable carbons are their low cost, their ability to be easily regenerated and (unlike other adsorbents such as zeolites or MOFs) their

hydrophobicity, which allows them to deliver an appropriate performance under wet conditions [González *et al.*, 2013].

1.5.3.1 CO_2 capture in postcombustion

So far, chemical absorption by aqueous-amine solutions is the most mature and industrially developed technology for CO_2 capture in power plants. However, this technology presents several drawbacks, such as corrosion rate and high energy requirements for regeneration [Creamer and Gao, 2016]. On the contrary, CO_2 capture by solid adsorbents (e.g. activated carbons) typically involves a weak bonding between CO_2 and the surface of the adsorbent, leading to lower energy requirements for the regeneration of the adsorbent. From a sustainability point of view, when the precursors used to prepare carbon-based adsorbents are lignocellulosic materials (or biochar produced from them), the attractiveness of these adsorbents is further enhanced.

For CO_2 capture in postcombustion, suitable adsorbents have to meet the following requirements [Hao *et al.*, 2013; Yang *et al.*, 2017]: (1) high CO_2 uptake at low CO_2 partial pressures (10–15 kPa), (2) high selectivity towards CO_2 over N_2 , (3) fast adsorption kinetic rate, and (4) low or moderate heat of adsorption. The CO_2 -over- N_2 selectivity of a porous sorbent can to a certain degree be determined by thermodynamic and kinetic reasons. Given that the molecule of CO_2 has a higher quadrupole moment ($-13.7 \times 10^{-24} \text{ cm}^2$) than that of N_2 ($-4.9 \times 10^{-26} \text{ cm}^2$), the interaction of CO_2 with the electrical field gradients of the sorbent is expected to be higher than that of N_2 . From the kinetics point of view, the effective kinetic diameter within porous solids of CO_2 is a little bit smaller than that of N_2 (0.33 and 0.36 nm, respectively). Hence, the diffusion rate of CO_2 into the pores of sorbents can be higher than that of N_2 , especially when the porous adsorbent has relatively uniform pores with sizes approaching the effective kinetic diameter of N_2 [Zhao *et al.*, 2015].

The main factor controlling the CO_2 uptake at low partial pressures of CO_2 (10–15 kPa) is the volume of ultra-micropores ($<0.7 \text{ nm}$) instead of the specific surface area [Hao *et al.*, 2013]. However, developing a certain mesoporosity in the activated carbon can enhance gas transport and diffusion into the ultra-micropores by reducing the resistance to mass transfer and shortening diffusion paths [Nelson *et al.*, 2016]. In addition to the role of hierarchical porosity, modifying the surface of the adsorbent with nitrogen functional groups can result in an enhancement of the adsorption

capacity of acidic gases such as CO_2 [Chen *et al.*, 2016]. Nevertheless, the effect of N-doping on the performance of CO_2 adsorption is still unclear. In fact, a marginal or even negligible effect was reported [Sevilla *et al.*, 2013]. Table 1.3 lists the CO_2 adsorption capacities at equilibrium (at 25°C and 15 kPa) recently reported in the literature for some advanced porous carbons produced from lignocellulosic precursors.

1.5.3.2 Biogas upgrading and hydrogen purification

In order to upgrade biogas (from anaerobic digestion) and landfill gas to natural gas quality, the main impurities (CO_2 , H_2O , and H_2S) should be removed through absorption, adsorption and/or membrane separation processes. The undesired compounds can be removed sequentially starting with H_2S and H_2O and ending with the separation of CO_2 and CH_4 [Zhou *et al.*, 2017].

The adsorption of H_2S on activated carbons represents an alternative to other available technologies for the removal of H_2S from raw biogas at relatively low concentrations (e.g. below 1000 ppm_v) [Castrillon *et al.*, 2016]. Chemical activation with basic compounds (such as NaOH, KOH and K_2CO_3) can result in a significant improvement in the H_2S sorption capacity as a consequence of the involvement of a chemisorption mechanism. Impregnation of carbonaceous precursors with Fe_2O_3 was also reported to be an effective measure to increase the H_2S uptake [Bagreev *et al.*, 2001]. Recently, Hervy *et al.* [2018] reported excellent H_2S adsorption capacities (in dry conditions and room temperature) for biomass-derived chars, which were physically activated with steam. The authors also revealed that these low-cost and renewable H_2S adsorbents exhibited the following properties: high specific surface area with large mesoporous volume, alkaline pH surface, presence of mineral species on the surface (especially Ca, Al, Fe), O-containing functional groups (especially basic groups) and disorganized carbonaceous structure.

Regarding the selective adsorption of CO_2 over CH_4 , pressure swing adsorption (PSA) processes have received growing attention, due to their energy and cost efficiency. Given that the PSA units usually operate at pressures ranging from 0.4 to 1.0 MPa, the performance of a given porous carbon, in terms of CO_2 uptake and selectivity towards CO_2 over CH_4 , should be assessed at much higher absolute pressures than those applied in postcombustion CO_2 capture approaches. For instance, Álvarez-Gutiérrez *et al.* [2016] observed a good performance (especially at an

Table 1.3: CO₂ uptakes at 25°C and 15 kPa reported for porous carbons derived from different precursors.

References	Highest CO ₂ uptake reported (mmol g ⁻¹)	Precursor	Preparation method
Hao <i>et al.</i> [2013]	1.10	HTC chars from grass cuttings	Physical activation with CO ₂ at 800°C.
Manyà <i>et al.</i> [2018]	1.22	Pyrolyzed vine shoots at 600°C under N ₂	Physical activation with CO ₂ at 800°C (3 h soaking time).
Li <i>et al.</i> [2015]	1.55	Pyrolyzed rice husks at 520°C under N ₂	Chemical activation with KOH: wet impregnation at a mass ratio of 1:1 and subsequent heating under N ₂ at 710°C.
Yang <i>et al.</i> [2017]	1.45	Pyrolyzed coconut shells at 500°C under N ₂	Chemical activation with KOH: wet impregnation at a mass ratio of 1:1 and subsequent heating under N ₂ at 600°C.
Chen <i>et al.</i> [2016]	1.40	Pyrolyzed coconut shells at 500°C under N ₂	Modification of the precursor by urea (a mixture at a mass ratio of 1:1 was heated in air at 320°C) and chemical activation of the resulting sample with KOH (wet impregnation at a KOH/precursor mass ratio of 3 and subsequent heating under N ₂ at 650°C).
Deng <i>et al.</i> [2014]	2.00	Pyrolyzed pine nut shells at 500°C under N ₂	Chemical activation with KOH: dry mixture at a KOH/precursor mass ratio of 2 and subsequent heating under N ₂ at 700°C.
González <i>et al.</i> [2013]	1.10	Almond shells	Single-step activation with CO ₂ at 800°C.
Guo <i>et al.</i> [2016]	1.35	Pyrolyzed coconut shells at 500°C under N ₂	Preoxidation with H ₂ O ₂ followed by ammoxidation (by a mixture of ammonia and air at the ratio of 1:10 at 350°C for 5 h). The resulting samples were then activated with KOH (wet impregnation at a mass ratio of 1:1 and subsequent heating under N ₂ at 600°C).
Parshetti <i>et al.</i> [2015]	1.20	HTC chars from empty fruit brunch at 350°C	Chemical activation with KOH: wet impregnation at a KOH/precursor mass ratio of 5 and subsequent heating under N ₂ at 800°C.
Serafin <i>et al.</i> [2017]	1.25	Pomegranate peels	Single-step activation with KOH: wet impregnation at a mass ratio of 1:1 and subsequent heating under N ₂ at 700°C.
Coromina <i>et al.</i> [2016]	1.50	HTC chars from Jujun grass at 350°C	Chemical activation with KOH: dry mixture at a KOH/precursor mass ratio of 2 and subsequent heating under N ₂ at 700°C.

absolute pressure of 0.5 MPa) of cherry stones-derived activated carbons (physically activated with CO₂ or steam) for the separation of CO₂/CH₄ under dynamic conditions in a packed-bed.

Hydrogen can be obtained using a number of different processes, such as steam methane reforming and thermochemical conversion of coal and/or biomass. However, the hydrogen produced also contains a high proportion of impurities, such as H₂O, CO, CO₂, CH₄ and, in some cases, N₂ [Delgado *et al.*, 2014]. The removal of these impurities can be performed using a PSA process, which is based on multilayer beds (at least 3) of different adsorbents. The first layer, which is usually composed of a hydrophilic adsorbent (e.g. alumina or silica gel), usually removes water vapor. In the second layer, the CO₂ is adsorbed using selective adsorbents, such as activated carbons; whereas the lighter compounds (e.g. CO and CH₄) are removed in a third layer, which is usually composed of zeolite-based adsorbents. So far, very few studies have focused on assessing the performance (in terms of capacity uptake and selectivity) of biochar-derived carbons for adsorption of CO₂ in a mixture of CO₂/H₂.

1.5.4 Biochar as catalyst or catalyst support

Carbon-based materials are widely used in the heterogeneous catalysis field because of their unique properties in terms of porosity and functional group tunability [Cao *et al.*, 2017]. As compared to non-renewable fossil fuel-derived carbonaceous materials, the production of biochar-derived materials is more sustainable and easily scalable. Thus, functionalized biochars have considerable potential to be used as direct catalysts or catalyst supports in several advanced applications. In this section, a brief overview is given on the utilization of biochar-derived materials as catalysts and/or catalyst supports in biomass upgrading processes.

1.5.4.1 Biochar-based solid acids

Biochar-containing sulfonic acid (SO₃H) groups, also called biochar-based solid acids, are considered as a type of metal-free catalyst that can be used in a wide variety of chemical processes. The most common way to synthesize amorphous carbon-based solid Brønsted acids is by surface sulfonation of biochar using sulfuric acid [Dehkhoda *et al.*, 2010]. Given the strong oxidation power of sulfuric acid, surface sulfonation can be accompanied by a production of oxygen-containing functionalities

(e.g. -COOH and phenolic -OH), which can enhance further the catalytic activity of the biochar-based solid acids [Hara, 2010].

Biochar-based solid acid catalysts can be applied in several processes aimed to produce valuable platform chemicals, such as furfural (FF) and 5-hydroxymethylfurfural (HMF), from biomass via the hydrolysis of cellulose and hemicelluloses and further dehydration of C_6 carbohydrates [Cao *et al.*, 2017]. Several studies have already highlighted that the biochar-based solid acids represent a promising alternative to mineral acids in biomass hydrolysis and dehydration, because they are cheaper, less corrosive and easier to recycle. For instance, Hu *et al.* [2015] reported an excellent activity of a magnetic lignin-derived solid acid catalyst for the dehydration of fructose into HMF. This catalyst was prepared through a three-step impregnation–carbonization–sulfonation process using the enzymatic hydrolysis lignin residue as precursor. By impregnation of FeCl_3 , carbonization at 400°C under N_2 atmosphere, and treatment with concentrated sulfuric acid, the resulting magnetic catalyst exhibited a relatively high surface area and contained Fe_3O_4 components, which were formed during the carbonization step. Interestingly, the Fe_3O_4 structure formed during the pyrolysis of the FeCl_3 -preloaded biomass was not seriously affected by the sulfonation step. Thus, the lignin-based catalyst was easily separated from the reaction mixture using a magnet.

Biochar-based solid acids can also be used in biodiesel production processes. For instance, Kastner *et al.* [2012] prepared acid catalysts (by sulfonating biochar with concentrated H_2SO_4 or gaseous SO_3) with very good performance in the esterification of fatty acids. Biochar-based solid acid catalysts also showed favorable performance in the catalytic transesterification of triolein and methanol [Zeng *et al.*, 2014].

1.5.4.2 Biochar-supported catalysts

It is well known that the presence of inherent inorganic compounds (especially alkaline and alkaline-earth metals, such as K, Ca and Na) in the biochar matrix can catalyze several reactions involved in the thermochemical conversion of biomass (e.g. pyrolysis and gasification). Manyà *et al.* [2016] reported a significant improvement of the pyrolysis gas (i.e. higher yields of CH_4 , H_2 and CO) when K_2CO_3 (5 wt.%) and CaO (5 wt.%) were added to a biomass feedstock (two-phase olive mill waste) during the slow pyrolysis of the given mixture at a peak temperature of

600°C. Wang *et al.* [2010] suggested that the *in situ* addition of K_2CO_3 promoted the decomposition of hemicelluloses, cellulose and lignin (the main biomass constituents), leading to increased yields of gaseous and biochar products at the expense of the pyrolysis liquid fraction. In other words, potassium accelerates the thermal decomposition and simultaneously promotes the secondary reactions of volatiles leading to an additional production of gas and biochar. Ren *et al.* [2014] also analyzed the *in situ* catalytic performance of a corn stover-derived biochar during the microwave pyrolysis of Douglas fir sawdust pellets at 480°C. Their results indicated that the biochar catalyst can significantly improve the quality of produced gas, since an increase in the yields of H_2 , CO and CH_4 was achieved.

In addition to the *in situ* role of the inherent inorganic constituents, biochar can also be used in a downstream catalytic bed reactor to upgrade the pyrolysis vapors. For instance, Wang *et al.* [2017] used a fixed-bed of a pyrolysis char from municipal solid waste (at a temperature of 500–600°C) to reform the pyrolysis vapors coming from the pyrolysis of the same precursor. They showed a good performance of this very cheap catalyst: approximately 60% of the moisture contained in the pyrolysis vapors was consumed in the reforming process, leading to an increased gas yield with a high carbon conversion ratio into produced gas.

On the other hand, biochar-derived materials have a great potential to be used as supports to stabilize metal nanoparticles for different catalytic applications. Biochar supported metals or metal oxides can be prepared by impregnating the biochar with metal precursors. An interesting single-step route was recently suggested to synthesize biochar-supported Ni/Fe catalysts with highly dispersed metal nanoparticles by impregnation with $Fe(NO_3)_3$ and $Ni(NO_3)_2$ onto a rice husk-derived biochar and subsequent calcination at 600°C [Shen *et al.*, 2014]. This catalyst showed a good performance in the removal of tar from a biomass gasifier (tar conversion efficiencies of around 93%). The biochar support can play a dual role: (1) It can act as a reduction media, converting metal oxides into metal nanoparticles, thus enhancing the catalytic activity; (2) The biochar itself can adsorb volatile compounds contained in the pyrolysis/gasification tar, thus also enhancing tar cracking and reforming reactions [Liu *et al.*, 2015]. Yao *et al.* [2016] also produced biochar-supported Ni catalysts, by impregnation of $Ni(NO_3)_2$ onto several biochars and further calcination at 800°C, to enrich the hydrogen content of a gas produced from biomass gasification at 800°C. The best catalytic performance was observed for

the Ni catalyst supported on a cotton stalk-derived biochar (H_2 content of 64 vol.% and H_2 yield of 92 mg g^{-1} of gasified biomass).

1.5.5 Biochar-derived materials for electrochemical energy storage

The efficient storage of energy in electrochemical energy storage devices (e.g. batteries or supercapacitors) appears to be crucial in moving from current energy supply sources (mainly based on fossil fuels) towards sustainable and renewable ones. Biochar-derived materials have a great potential to be used as electrode materials in energy storage devices, including lithium-ion batteries (LiBs), lithium-sulfur batteries (Li-SBs), sodium-ion batteries (SiBs) and supercapacitors.

1.5.5.1 Lithium-ion batteries

Graphite is currently the most widely used commercial anode material in lithium-ion batteries (LiBs). Nevertheless, graphite (having a theoretical specific capacity of 372 mA h g^{-1}) cannot meet the increasing demand for high capacity batteries. Despite the fact that biomass-derived carbonaceous materials have a great potential to be used as anodes in LiBs, their electrochemical performance depends, to a great extent, on the nature of the biomass precursor as well as the operating conditions adopted during the carbonization and activation processes. This fact can explain the wide variability in the performance indicators (such as specific capacity, capacity retention after a number of cycles and Coulombic efficiency) reported in the literature for several biomass-derived carbons. Some encouraging results from previous studies on developing biomass-based materials for LiBs' purposes are given in Table 1.4.

1.5.5.2 Lithium-sulfur batteries

With a theoretical energy density of 2600 W h kg^{-1} (3–5 times greater than that of the lithium-ion batteries [Marmorstein *et al.*, 2000]), lithium-sulfur batteries (Li-SBs) represent a very promising alternative for the next generation of rechargeable batteries. As a key component of a Li-S battery, the sulfur cathode contributes to the high energy density of the battery by delivering a remarkably high theoretical capacity of 1675 mA h g^{-1} .

Table 1.4: Summary of the results obtained in some published studies on the performance of biomass-derived carbons as anode material for LiBs.

References	Material	Specific capacity (discharge)
Han <i>et al.</i> [2014]	Biochar from tea leaves produced by pyrolysis at 700°C, atmospheric pressure and under an N ₂ atmosphere.	471 mA h g ⁻¹ at the 50th cycle (current density = 47.1 mA g ⁻¹)
Unur <i>et al.</i> [2013]	Hydrochar from hazelnut shells (produced at 250°C; soaking time = 7.5 h) thermally activated under Ar at 600°C.	300 mA h g ⁻¹ at the 100th cycle (current density = 300 mA g ⁻¹)
Yi <i>et al.</i> [2017]	Graphene-like carbon sheet (GCS) <i>in situ</i> doped GCS/Fe ₃ O ₄ nanocomposite from soda paper-making black liquor (impregnation of black liquor with an aqueous solution of Fe ³⁺ , hydrothermal treatment of the precursor solution at 180°C for 48 h, and thermal activation at 700°C under N ₂).	750 mA h g ⁻¹ at the 1400th cycle (current density = 1000 mA g ⁻¹)
Wang <i>et al.</i> [2014]	Carbon-Co ₃ O ₄ nanocomposites from pyrolyzed crawfish shells (at 700°C under N ₂) and subsequent hydrothermal treatment (at 150°C for 3.5 h) of a solution of a mixture of the char precursor (previously dissolved in ethanol) and an aqueous solution of Co(CH ₃ COO) ₂ ·4H ₂ O.	1060 mA h g ⁻¹ at the 100th cycle (current density = 100 mA g ⁻¹)

However, there are still some drawbacks limiting the further development and implementation of Li-SBs (e.g. poor rate performance, capacity fading and low Coulombic efficiency) [Yang *et al.*, 2015].

Using porous carbon-based sulfur composites as cathode materials can significantly improve the performance of Li-SBs because the high electronic conductivity and electrochemical affinity for sulfur of porous carbons [Ye *et al.*, 2013]. The porosity of the carbon matrix is a key factor explaining the performance of the cathode. In this sense, it seems appropriate to develop porous carbons with hierarchical structures containing

both micro- and meso-porosity. Micropores are able to adsorb the migrating polysulfides, thus avoiding their dissolution into the electrolyte. For their part, mesopores can facilitate lithium-ion transport and ensure appropriate accessibility to the electrolyte during the course of the electrochemical reactions involved [Zhang *et al.*, 2017]. Numerous studies already focused on developing high-performance cathode materials from biomass. Table 1.5 summarizes the performance of several biomass-based materials tested in Li-SB applications.

1.5.5.3 Sodium-ion batteries

In the last few years, sodium-ion batteries (SiBs) have gained growing attention as a low-cost alternative to LiBs because of the abundance of sodium resources throughout the world. Due to the fact that Na-ion has a larger ionic radius than that of Li-ion, one of the key challenges for SiBs' development is to use anode materials having appropriate space for intercalating and accommodating Na-ions [Gao *et al.*, 2018]. Engineered hard carbons (i.e. highly disordered and non-graphitizable carbons) are strong candidates to be used as anodes in SiBs. Using hard carbons, sodium ions can be stored in randomly stacked graphene layers and micropores.

Several hard carbons have recently been prepared from biomass sources (such as banana peels [Lotfabad *et al.*, 2014], pomelo peels [Hong *et al.*, 2014], and lignin [Li *et al.*, 2016]) and tested as anodes for SiBs. Anodes based on large surface area carbonaceous materials (with relatively large volumes of mesopores) can deliver a relatively high capacity and good rate performance, as a consequence of the broad contact between electrolytes and electrodes, which results in a fast transfer of electrons and Na-ions [Zheng *et al.*, 2016]. Nevertheless, their capacities after the first cycle can dramatically decrease, due to the formation of the solid-electrolyte interphase (SEI) [Hong *et al.*, 2014; Zheng *et al.*, 2016]. Alternatively, using hierarchical porous carbons having large micropore volumes and limited mesoporosity can lead to higher initial Coulombic efficiencies (i.e. ratio of the total charge extracted from the battery to the total charge put into the battery over a full charge cycle) with appropriate specific capacities. In other words, tuning the porous structure of the biomass-derived carbons is a key step during the preparation of anode materials for SiBs. The electrochemical performances of some biomass-derived anode materials for SiBs are summarized in Table 1.6.

Table 1.5: Summary of the results obtained in some published studies on the performance of biomass-derived carbons as cathode materials for Li-SBs.

References	Material	Specific capacity (discharge)	Capacity retention
Guo <i>et al.</i> [2015]	Sulfur/Porous carbons nanosheet (S/PCNS) composites. PCNS were obtained from corncob by carbonization (at 500°C), wet impregnation with KOH, and thermal activation (in Ar at 900°C). Sublimed sulfur was then added to PCNS by physical mixture and subsequent heating in two steps (at 155°C for 12 h and at 300°C for 2 h).	634 mA h g ⁻¹ at the 50th cycle (current density = 63.4 mA g ⁻¹)	39.6% at the 50th cycle
Yang <i>et al.</i> [2015]	Sulfur/activated carbon (S/AC) composites. AC was obtained from apricot shells by KOH activation (at 750°C under Ar). Sublimed sulfur was then added to AC by physical mixture and subsequent heating (at 155°C for 15 and at 300°C for 0.5 h).	733 mA h g ⁻¹ at the 200th cycle (current density = 146.6 mA g ⁻¹)	61.4% at the 200th cycle
Zhang <i>et al.</i> [2014]	Sulfur/activated carbon (S/AC) composites. AC was obtained from litchi shells by carbonization (at 500°C) and subsequent KOH activation (at 900°C under Ar). Sublimed sulfur was then added to AC by physical mixture and subsequent heating at 155°C for 12 h.	665 mA h g ⁻¹ at the 100th cycle (current density = 800 mA g ⁻¹)	72.5% at the 100th cycle
Chen <i>et al.</i> [2017]	Sulfur/hierarchical porous carbon (S/LC) composites decorated by ionic surfactants. Porous carbon was obtained from lotus seedpod shells by carbonization (in Ar at 800°C) and subsequent KOH activation (at 850°C under Ar). Sulfur and ionic surfactants were then added to the porous carbon (sulfur content = 86.5%).	1160 mA h g ⁻¹ at the 100th cycle (current density = 116 mA g ⁻¹)	84.0% at the 100th cycle

Table 1.6: Summary of the results obtained in some published studies on the performance of biomass-derived carbons as anode materials for SiBs.

References	Material	Specific capacity (discharge)	Initial Coulombic efficiency (%)
Lotfabad <i>et al.</i> [2014]	Carbonization (slow pyrolysis) of banana peels at 1100°C for 5 h under Ar. The produced carbon exhibited a very low S_{BET} (19.3 m ² g ⁻¹ ; deduced from the adsorption isotherm of N ₂ at 77 K). The authors stated that this material was composed of pseudographitic arrays possessing a mean graphene interlayer spacing that was 17% dilated with respect to graphite, allowing for facile Na intercalation between the layers.	300 mA h g ⁻¹ at the 290th cycle (current density = 100 mA g ⁻¹); with a capacity retention of 88%	67.8
Hong <i>et al.</i> [2014]	Carbonization of dried pomelo peels, previously impregnated with H ₃ PO ₄ , at 700°C for 2 h under N ₂ . A high S_{BET} of 1272 m ² g ⁻¹ was reported. Pore size distribution also indicated a high proportion of mesopores in the range of 4–23 nm.	181 mA h g ⁻¹ at the 220th cycle (current density = 200 mA g ⁻¹); with a capacity retention of 84.6%	27.0
Li <i>et al.</i> [2016]	Carbonization of a mixture of pitch and lignin (mass ration of 1:1) at 1400°C for 2 h under Ar. A very small S_{BET} of 1.34 m ² g ⁻¹ was deduced from the adsorption isotherm of N ₂ at 77 K, indicating a narrow microporous nature of the material.	226 mA h g ⁻¹ at the 150th cycle (current density = 30 mA g ⁻¹); with a capacity retention of 89%	82.0
Wang <i>et al.</i> [2017]	Carbonization of milled mangosteen shells at 1500°C for 2 h under Ar. A very small S_{BET} of 8.9 m ² g ⁻¹ was deduced from the adsorption isotherm of N ₂ at 77 K, indicating a narrow microporous nature of the material.	330 mA h g ⁻¹ at the 100th cycle (current density = 20 mA g ⁻¹); with a capacity retention of 98%	83.0

Table 1.7: Summary of the results obtained in some published studies on the performance of biomass-derived carbons as electrode materials for ECs.

References	Material	Specific capacitance	Capacity retained
Peng <i>et al.</i> [2018]	A mixture of coconut shell and sewage sludge was hydrothermally treated at 220°C for 3 h. The resulted hydrochar was then activated with KOH by dry mixture at a KOH/precursor mass ratio of 3 and subsequent heating at 700°C for 3 h under N ₂ . A very high S_{BET} of 3000 m ² g ⁻¹ was reported (total pore volume = 2.06 cm ³ g ⁻¹).	420 F g ⁻¹ at 0.5 A g ⁻¹ (three-electrode configuration; 6.0 M KOH aqueous solution as electrolyte).	94.5% after 10000 cycles (current density = 5 A g ⁻¹)
Choi <i>et al.</i> [2018]	Dried coffee grounds were carbonized at 700°C for 2 h under Ar. The resulting char was mixed with KOH at a mass ratio KOH/char of 6 and subsequently pyrolyzed at 700°C for 2 h under Ar (S_{BET} = 2620 m ² g ⁻¹). Graphene oxide (GO) was finally dispersed at a concentration of 1.8 wt.% by chemical exfoliation of graphite.	512 F g ⁻¹ at 0.5 A g ⁻¹ (two-electrode symmetric configuration; 6.0 M KOH aqueous solution as electrolyte).	87% after 10000 cycles (current density = 5 A g ⁻¹)
Kang <i>et al.</i> [2018]	Rapeseed dregs and ZnCl ₂ were mixed at a mass ratio ZnCl ₂ /precursor of 4. The resulting mixture was then heated under N ₂ at 600°C for 1 h. To remove impurities, the obtained carbon was washed by 2 M HCl (S_{BET} = 1119 m ² g ⁻¹ ; total pore volume = 1.25 cm ³ g ⁻¹).	170 F g ⁻¹ at 0.5 A g ⁻¹ (3-electrode configuration; 1.0 M H ₂ SO ₄ aqueous solution as electrolyte).	90% after 6400 cycles (current density = 1 A g ⁻¹)
Gao <i>et al.</i> [2016]	Shrimp shell and KOH with a mass ratio of 1:4 were thoroughly mixed and then pyrolyzed at 700°C for 1 h in an atmosphere of Ar. To remove CaCO ₃ , the obtained carbons were dissolved in acetic acid. The CaCO ₃ -free samples were finally washed with deionized water until the solution became neutral (S_{BET} = 1113 m ² g ⁻¹ ; total pore volume = 0.68 cm ³ g ⁻¹).	300 F g ⁻¹ at 0.5 A g ⁻¹ (3-electrode configuration; 6.0 M KOH aqueous solution as electrolyte).	93.6% after 1000 cycles (current density = 1 A g ⁻¹)

1.5.5.4 Supercapacitors

Electrochemical capacitors (ECs), also known as supercapacitors, have attracted great attention due to their high power capability, fast discharge rates, long cycling life and relatively low maintenance cost [Choi *et al.*, 2018]. So far, one of the main challenges in developing ECs is to improve the energy density without reducing the power density and/or cycling life.

Biomass-derived porous carbons are strong candidates to be used as a main electrode material in ECs. More in detail, biomass-derived carbons having large specific surface areas and well-developed hierarchical porous structure (i.e. containing micro-, meso- and macropores), and heteroatoms (doped with e.g. N, S, and B) seem to be highly appropriated for ECs [Kang *et al.*, 2018]. The presence of macropores can result in a faster ionic diffusion at the internal surface of porous carbons, whereas mesopores can act as channels to enhance the transportation of ions. For its part, a large micropore volume can provide the required locations for charge accommodation. In other words, a hierarchical pore size distribution is highly recommended in order to reach a high rate performance and power density (due to the accelerated ion transfer through the macro- and mesopores) and, at the same time, a high specific capacitance and energy density (given the large ion-accommodating surface area in the micropore region) [Feng *et al.*, 2016]. In addition, introducing heteroatoms into the carbon framework can result in a higher pseudo-capacitance caused by faradaic reactions from the heteroatom, leading to an improvement of both specific capacitance and rate performance [Gao *et al.*, 2016; Kang *et al.*, 2018]. Some examples of the performance of biomass-derived porous carbons in ECs are summarized in Table 1.7. Chapter 7 provides a more detailed overview of the potential of biomass-derived carbons as electrode components for ECs.

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